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Sulfonated Polybenzothiazoles: A Novel Candidate for Proton Exchange Membranes†

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Sulfonated polybenzothiazoles (sPBT) with high molecular weight as well as excellent solubility were synthesized for the first time, which was achieved by attaching the phenylsulfonyl pendant groups or incorporating the hexafluoroisopropylidene moieties to the polymer backbone. Such sulfonated polybenzothiazoles thus could be cast into homogeneous membranes and could be further evaluated as proton exchange membranes. These sPBTs showed high thermal stability and high proton conductivity as well as low swelling. For instance, the hexafluoroisopropylidene-containing sPBT with a disulfonation degree of 65% exhibited a T_{d5} of 380 °C, a proton conductivity of 0.11 S/cm, and a swelling of 15.5% at 80 °C. In addition, the sPBT membranes showed excellent oxidative and hydrolytic stability. In comparison with the phenylsulfonyl pendant-group-containing sPBT membranes, the hexafluoroisopropylidene-containing sPBT membranes with an equivalent ion exchange capacity showed much narrower ionic channels because of the hydrophobic hexafluorisopropylidene moieties. This made the latter display better dimensional stability, oxidative stability, and hydrolytic stability than the former. This investigation illustrated that sulfonated polybenzothiazoles are a novel candidate for proton exchange membranes.

Introduction

As a green power device, proton exchange membrane fuel cell (PEMFC) has attracted increasing attention in recent years. A proton exchange membrane (PEM) is one of the key components of PEMFC, and perfluorinated membranes such as Nafion are the reference membrane for PEMFC. However, the drawbacks such as low operating temperature, high methanol permeability, and high cost seriously limited their application in fuel cells.[1] Therefore, intensive efforts have been made to develop aromatic proton exchange membranes and composite membranes.[1−8] Wholly aromatic polymers are regarded as one of the promising matrix for PEM because of their availability, wide variety of chemical compositions, and anticipated stability in the fuel cell environments. For example, poly(arylene ether)s,[9−11] poly(arylene thioether)s,[12−15] poly(phthalazinone ether)s,[16−18] polyimides,[19−22] polyphosphazenes,[23,24] and their derivatives[1] are the focus of recent investigations on PEM. More and more aromatic polymers were considered to be used as the bulk materials for PEM.

Aromatic polybenzazoles such as polybenzimidazoles (PBI), polybenzoxazoles (PBO), and polybenzothiazoles (PBT) are also high performance polymers,[25−27] thus they

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are of great interest to be used as the matrix of PEM. PBI-based proton exchange membranes have been intensively developed.[25,28−36] Polybenzoxazole based membranes have also been investigated for PEM applications.[37−39] However, few polybenzothiazoles have been studied as proton exchange membrane materials because of their poor processability.[40−43] Great attempts have been put forth to enhance their solubility by incorporating the bulky pendant groups or flexible linkage into the resulting polybenzothiazoles, but the result was not satisfactory.[44−47]

On the other hand, though polybenzothiazoles have high tensile strength, tensile modulus, and thermal stability, they showed poor compressive properties in addition to poor processability.[26,27] These disadvantages heavily limited their applications. To overcome these drawbacks, polybenzothiazoles with sulfonic acid groups were prepared by direct polycondensation.[48−50] The as-synthesized polymers were used as structural materials and were not evaluated as proton exchange membranes.[49,50] Furthermore, few studies relevant to sulfonated polybenzothiazoles were reported. It could also be found that the characterization of their structure and properties is very limited and that sPBT with high molecular weight as well as good solubility have not been reported until now. In addition, sulfonated polybenzothiazoles exhibit no softening behavior and glass transition prior to thermal degradation because of their rigid structure and strong intermolecular interaction like polybenzothiazoles,[26,49] and thus sPBT could not form homogeneous membrane by extrusion or by blow molding. Accordingly, the sPBT membranes for PEM applications might be prepared only by casting polymer solution. This demands that sulfonated polybenzothiazoles exhibit good solubility as well as high molecular weight in order to obtain good processability and mechanical properties. As a result, it is significant to synthesize such sulfonated polybenzothiazoles and to evaluate whether they could be employed as PEM materials or not.

In this article, sulfonated polybenzothiazoles were prepared by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride and bis(3-sulfonate-4-carboxyphenyl) sulfone with bis(4-carboxyphenyl) sulfone or diphenyl sulphone-2,5-dicarboxylic acid or 2,2-bis(4-carboxyphenyl)hexafluoropropane. The effects of the structural moieties such as diphenyl sulfone, hexafluoroisopropylidene, and phenylsulfonyl pendant groups on the properties of the resulting polymers were investigated. The incorporation of the phenylsulfonyl pendant groups or the flexible hexafluoroisopropylidene moieties to the resulting sulfonated polybenzothiazoles was expected to enhance the solubility and to achieve high molecular weight products. In this case, such sulfonated polybenzothiazoles could be cast into homogeneous membranes and could be further investigated as PEM. Their structure and properties as PEM, especially their solubility, swelling, hydrolytic stability, oxidative stability, and proton conductivity, were studied in detail so as to evaluate whether they are a promising PEM material or not.

Experimental Section

Materials. 2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT) was purchased from TCI and used as received. Bis(4-carboxyphenyl) sulfone (BCPS) and 2,2-bis(4-carboxyphenyl)hexafluoropropane (6FA) were obtained from ABCR and Sigma-Aldrich, respectively. Phosphorus pentoxide (corrosive), polyphosphoric acid (PPA, 81%), methane sulfonic acid (MSA, corrosive), benzene sulphonyl chloride (corrosive), *p*-xylene, aluminum chloride, triethylamine, and other chemicals were purchased from Shanghai Chemical Reagents Co. and used without further purification. Bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCS) was synthesized according to our previous report.[51]

Synthesis of Diphenyl Sulfone-2,5-dicarboxylic Acid. 2,5-Dimethyl diphenyl sulfone (DMPS) was synthesized by an aluminum chloride catalyzed Friedel−Crafts acylation reaction of benzene sulfonyl chloride with *p*-xylene following previous reports.[52−54] Diphenyl sulfone-2,5-dicarboxylic acid (PSCA) was prepared by oxidation of DMPS with potassium permanganate. The preparation procedure is as follows. Ten grams of DMPS, 4 g of sodium hydroxide, and 650 mL of deionized water were placed in a three-necked round-bottom flask. Potassium permanganate (36 g) was added in small portions over a period of 1 h. After refluxing for 24 h, the hot mixture was cooled and

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filtrated. The filtrate was acidified with 6 M sulfuric acid and then the precipitation appeared. Finally, the white product was obtained by filtration followed by washing with deionized water.

Yield: 90%. ^{1}H NMR (DMSO-d_6, ppm): 13.87 (s, 2H), 8.53 (s, 1H), 8.24 (d, $J = 8$, 1H), 7.96 (d, $J = 7.2$, 2H), 7.76 (d, $J = 8$, 1H), 7.69 (t, $J = 7.2$, 1H), 7.61 (t, $J = 6.8$, 2H). ^{13}C NMR (DMSO-d_6, ppm): 168.39, 165.97, 141.22, 138.67, 138.58, 135.22, 134.57, 133.64, 130.86, 130.15, 130.10, 128.43. FT-IR (KBr, cm^{-1}): 3450−2550, 1747 (−COOH), 1310, 1146 ($-SO_2-$).

Synthesis of sPBT. As a typical procedure, the preparation of sPBT-6F65 was depicted as follows. To a 50 mL three-necked round-bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer, PPA (12.4 g) and DABDT (0.45 g, 1.8352 mmol) were added. The mixture was stirred at room temperature for 12 h and then held at 70 °C for 36 h until the evolution of hydrogen chloride ceased. After cooling to room temperature, BSCS (0.6088 g, 1.1929 mmol) and 6FA (0.2519 g, 0.6423 mmol) were added to the clear reaction system and stirred at 100 °C for 8 h. Subsequently, an additional phosphorus pentoxide (3.8 g) was added, the mixture was heated as follows: 130 °C for 8 h, 150 °C for 10 h, 170 °C for 10 h, 190 °C for 12 h, and 210 °C for 12 h. The viscous solution was cooled to 140 °C and poured into deionized water to give yellow-green fibrous polymer. The product was washed with deionized water several times to remove residual acid, then soaked in 0.5 wt % $NaHCO_3$ solution overnight and washed until achieving a neutral pH, followed by drying in vacuo at 120 °C for 24 h.

Yield: 96%. ^{1}H NMR (DMSO-d_6): 8.92−8.86, 8.83, 8.50, 8.32−8.23, 8.14−8.06, 8.05−7.98, 7.65−7.54. FT-IR (KBr, cm^{-1}): 1630 (C=N), 1487, 1396, 1317 (benzothiazole ring stretching), 958 (benzothiazole ring breathing), 740 (benzothiazole ring deformation), 1088, 1014, 632 ($Ar-SO_3Na$).

Preparation and Acidification of Membrane. The sPBT polymer in the sodium salt form was dissolved in NMP. The solution (5 wt %) was cast onto a clean glass substrate and dried at 70 °C for 36 h. After cooling, the membrane was peeled off from the glass plate by immersion in deionized water, then acidified by soaking in 1 M HCl solution for 48 h and rinsed three times with deionized water to remove the free acid within the membrane.

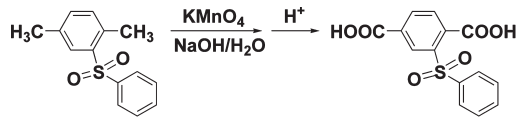
Characterization of Polymer and Membrane. FT-IR spectra were performed on a PE Paragon 1000 IR spectrometer. NMR spectra were recorded using a Mercury Plus 400 MHz NMR instrument. Gel permeation chromatography (GPC) was carried out on a PE 200 apparatus with DMF containing 0.05 M LiBr as eluent. Molecular weight was calibrated with polystyrene standards.

The thermogravimetric analysis (TGA) was measured on a PE TGA-7 thermogravimetric analyzer in air. Samples in the acid form were heated at 150 °C for 30 min to remove the moisture, followed by heating to 800 at 10 °C/min. Differential scanning calorimeter (DSC) measurements were conducted on a PE Pyris-1 apparatus. Samples in the acid form were preheated to 150 °C for 30 min under nitrogen and then cooled to 90 °C. DSC curves were recorded in a temperature range of 90−400 at 10 °C/min.

Ion exchange capacity (IEC) was determined by titration. The membrane in the acid form was immersed in saturated NaCl solution for two days in order to release H^+ by ion exchange. The released H^+ ions were titrated with 0.01 M NaOH.

The water uptake and swelling were obtained by changes in weight and length of the membrane from wet to dry state, respectively. The sample was immersed in deionized water at defined temperatures for 24 h, and then taken out and wiped with tissue paper before the weight and length were measured. The results were calculated by the following equations:

Scheme 1. Synthesis of PSCA



$$\text{water uptake} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%,$$
$$\text{swelling} = (L_{\text{wet}} - L_{\text{dry}})/L_{\text{dry}} \times 100\%$$

where W_{wet} and W_{dry} are the weight of the wet and dry membrane and L_{wet} and L_{dry} are the length of the wet and dry membrane, respectively.

The measurement of proton conductivity was conducted on a PARSTAT 2273 Advanced Electrochemical System in the frequency range of 10−10^6 Hz with an oscillating voltage of 10 mV. The proton conductivity (σ) was calculated by the formula of $\sigma = L/(RA)$, where R, L, and A are the resistance, the distance between two electrodes, and the cross-sectional area of membranes, respectively.

The oxidative stability was investigated following a typical procedure.[55] In the course of test, a small piece of membrane sample (0.5 cm × 1 cm) with a thickness about 40 μm was soaked in Fenton's reagent (2 ppm $FeSO_4$ in 3% H_2O_2) at 80 °C. The oxidative stability was evaluated by recording the residual weight of the membrane after treatment in Fenton's reagent for 1 h and the elapsed time when the membrane disappeared completely.

The hydrolytic stability was investigated by treating the membrane sample in water at 140 °C for 24 h as a typical accelerated testing.[55] The hydrolytic stability was evaluated by changes in mechanical properties, residual weight, molecular weight, FT-IR spectra, and ^{1}H NMR spectra of the samples. Mechanical properties were tested with an Instron 4456 instrument at ambient conditions (25 °C and 50% relative humidity) at a crosshead speed of 1 mm/min. The wet samples for testing mechanical properties were equilibrated at ambient conditions for 24 h before measurement according to a well-established procedure.[56]

Atomic force microscopy (AFM) imaging was performed on a Digital Instruments Nanoscope III in tapping mode. All samples in the acid form were dried at 70 °C for 24 h. The samples were imaged under ambient conditions.

Results and Discussion

Synthesis of Diphenyl Sulphone-2,5-dicarboxylic Acid. 2,5-Dimethyl phenyl sulfone (DMPS) was synthesized by Friedel−Crafts acylation reaction of benzene sulfonyl chloride with *p*-xylene. In the previous reports, diphenyl sulphone-2,5-dicarboxylic acid (PSCA) was prepared by oxidation of 2,5-dimethyl phenyl sulfone with nitric acid,[52−54] which was carried out in a stainless steel autoclave under high temperature (160−190 °C) and high pressure. A mild alternative route was given in this paper. Diphenyl sulphone-2,5-dicarboxylic acid was easily synthesized by oxidation of DMPS using potassium permanganate as

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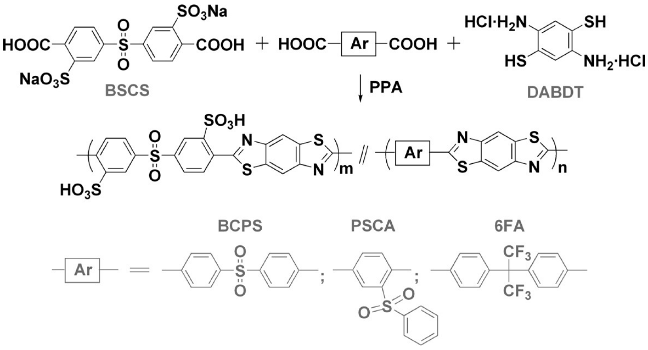
Scheme 2. Preparation of sPBT



oxidative reagent in refluxing NaOH solution, as shown in Scheme 1. The structure of PSCA was confirmed by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy.

Synthesis of sPBT. Three series of sPBT with various degrees of sulfonation were prepared by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCS) with one of the unsulfonated monomers such as bis(4-carboxyphenyl) sulfone (BCPS), diphenyl Sulphone-2,5-dicarboxylic acid (PSCA), and 2,2-bis(4-carboxyphenyl)hexafluoropropane (6FA), respectively, as indicated in Scheme 2. sPBT derived from BCPS, PSCA, and 6FA are denoted as sPBT-BCxx, sPBT-PSxx, and sPBT-6Fxx, respectively, where the "xx" is the molar percentage of BSCS in the dicarboxylic monomers. The polymerization reaction was carried out in polyphosphoric acid at a solid content of 6 wt %. In the initial stage of polycondensation reaction, the temperature was kept at 100−150 °C for several hours to completely remove hydrogen chloride in the mixture, which is critical for achieving high molecular weight products as mentioned in the literature.[46,57] The results of polycondensation reaction are summarized in Table 1. As shown, all the copolymers, except for sPBT-BC50, exhibited a number average molecular weight higher than 6×10^4 g/mol, and their polydispersity index (PDI) was in the range of 1.6−3.0, suggesting that high molecular weight sPBT polymers were successfully prepared. In addition, the sPBT-6F and sPBT-PS series could be cast into transparent, tough, and ductile membranes, further confirming that they showed high molecular weight. It is noticeable that sPBT-BC50 showed only partial solubility in DMF, so its molecular weight and polydispersity index could not be obtained by GPC, but the number average molecular weight of its soluble part is still higher than 6×10^4 g/mol, showing high molecular weight.

As typical examples, the ^{1}H NMR spectra of sPBT-6F65, sPBT-BC65, and sPBT-PS65 in DMSO-d_6/LiCl is shown in Figure 1. LiCl was used to reduce the intermolecular association.[32] As shown, the signal peaks were well-assigned. The chemical shift of H_1, H_2, H_3, and H_4 atoms in the sulfonated repeat units of sPBT-6F65 is close to that of H_1, H_2, H_3, and H_4 atoms in the sulfonated repeat units of sPBT-BC65 and sPBT-PS65, respectively. This is because the H atoms in the identical position of sulfonated repeat units have a similar chemical environment and thus show the approximate chemical shift. The ^{1}H NMR spectra of sPBT-6F65, sPBT-BC65, and sPBT-PS65 confirmed their chemical structure. The assignment of ^{1}H NMR spectra of these sPBT polymers was analyzed in Figure S1 in the Supporting Information.

The IR absorptions of polybenzothiazoles were extensively investigated in the past.[45,58] The IR spectra of all the products are shown in Figure S2 in the Supporting Information. As shown, there is no residual absorption band at 2600−2500 cm^{-1} (-SH) and 1750−1650 cm^{-1} (C═O), suggesting that the cyclization of benzothiazole units is complete. The absorptions at 1487, 1396, 1317, and 958 cm^{-1} are assigned to the characteristic vibration of benzothiazole rings, and the peak at 740 cm^{-1} is ascribed to the deformation of benzothiazole rings. Besides, the characteristic bands related to $-SO_3Na$ are located at 1088, 1014, and 632 cm^{-1}.[14,16] Therefore, the chemical structure of sPBT was further confirmed by FT-IR spectroscopy.

Thermal Properties of sPBT. The thermal stability of the products was determined by TGA technique in air. The TGA traces of the resulting polymers are presented in panel ***a*** and ***b*** of the Figure 2, and the 5% weight loss temperature (T_{d5}) is listed in Table 1. As illustrated in Figure 2, all the sPBT polymers displayed a typical two-step degradation profile.[14] The first weight loss starting from 350 °C belongs to the decomposition of sulfonic acid groups, and the second weight loss at 480 °C is related to the degradation of polymer backbone. All the sPBT displayed no residue in air at 700 °C. This illustrated that they were completely converted to the acid form by ion exchange. As seen in Table 1, all the sPBT polymers exhibited a T_{d5} no lower than 380 °C, showing high thermal stability. For each series of sPBT, the T_{d5} decreased slightly as the degree of sulfonation rises, similar to the previous reports.[14,16] This is due to the fact that the first weight loss was caused by degradation of sulfonic acid groups.

The glass transition temperature of sPBT polymers was measured by DSC. However, they showed no glass transition, no exothermal peak, and no endothermal peak in the range of 90−350 °C (see Figure S3 in the Supporting Information), similar to the rigid rod polybenzothiazoles.[26]

Solubility of sPBT. As mentioned above, sulfonated polybenzothiazoles exhibited no glass transition and melting behavior prior to thermal degradation, so homogeneous sPBT membrane might only be obtained by solution casting. Consequently, it is necessary for sPBT to possess high solubility so as to prepare the membranes used as PEM. The solubility of sPBT polymers was tested at a concentration of 0.05 g/mL, and the results are presented in Table 2. As shown, all the sPBT polymers exhibit no solubility in methanol and water. The sPBT-BC

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Table 1. Polycondensation Results and Properties of sPBT

		GPC					IEC (meq/g)		
polymer	BSCS/BCPS/PSCA/6FA (molar ratio)	Mn × 10^{-4} (g/mol)	M_w × 10^{-4} (g/mol)	PDI	yield (%)	T_{d5} (°C)	the calculated	the measured	λ^c (H_2O/SO_3H)
sPBT-BC50	50/50/0/0	6.26[a]	12.5[a]	1.99[a]	90	395	2.06	[b]	[b]
sPBT-BC65	65/35/0/0	6.01	10.4	1.73	93	385	2.55	[b]	[b]
sPBT-PS50	50/0/50/0	9.89	18.7	1.89	93	393	2.06	2.00	11.8
sPBT-PS55	55/0/45/0	8.51	13.8	1.63	95	392	2.22	2.15	11.5
sPBT-PS60	60/0/40/0	13.8	30.3	2.18	94	389	2.39	2.30	12.2
sPBT-PS65	65/0/35/0	7.61	21.9	2.89	96	385	2.55	2.49	13.5
sPBT-PS70	70/0/30/0	6.80	17.0	2.50	95	382	2.70	2.60	14.2
sPBT-6F50	50/0/0/50	7.32	21.9	3.00	94	395	1.89	1.81	10.2
sPBT-6F55	55/0/0/45	6.85	20.2	2.95	92	391	2.06	2.01	10.0
sPBT-6F60	60/0/0/40	6.70	19.5	2.91	94	385	2.23	2.15	10.0
sPBT-6F65	65/0/0/35	6.69	19.9	2.98	95	380	2.40	2.31	10.2

[a] The values are the results of the soluble part. [b] Difficult to obtain because of its poor solubility. [c] The hydration number (number of H_2O molecules per sulfonic acid group) at 80 °C.

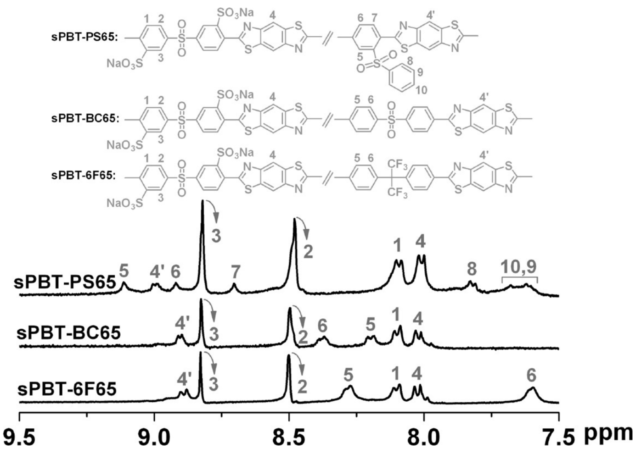

Figure 1. ^1H NMR spectra of sPBT-PS65, sPBT-BC65, and sPBT-6F65.

series derived from bis(4-carboxyphenyl) sulfone, i.e., sPBT-BC50 and sPBT-BC65, exhibited the poorest solubility among all the products, only partially soluble in the aprotic polar solvents even on heating, and hence they could not be cast into the homogeneous membrane used as PEM. Generally, the rigid rod polybenzothiazoles show no solubility in any of those solvents even on heating.[40−42] However, the sPBT-BC series still exhibited some solubility, which is ascribed to the steric effect and ionization of sulfonic acid pendant groups. In contrast, the sPBT-PS series (sPBT-PS50−PS70) containing phenylsulfonyl side groups displayed excellent solubility in NMP, DMSO, and DMF. This is because the phenylsulfonyl pendant groups of sPBT inhibit the chain packing and increase intermolecular space and thus enhance the solubility of products. On the other hand, the sPBT series with hexafluoroisopropylidene moieties such as sPBT-6F50, -6F55, -6F60, and -6F65 were readily soluble in NMP, DMSO, and DMF. This illustrated that the flexible hexafluoroisopropylidene moieties is favorable to increase the solubility of the resulting sPBT. In conclusion, the excellent solubility of sPBT polymers has been achieved by attaching the bulky pendant groups or incorporating flexible moieties to polymer backbone. High-molecular-weight sPBT polymers (sPBT-PS and sPBT-6F series) with excellent solubility have been prepared for the first time. Such sulfonated polybenzothiazoles could be cast into homogeneous membranes and thus could be further evaluated as PEM materials.

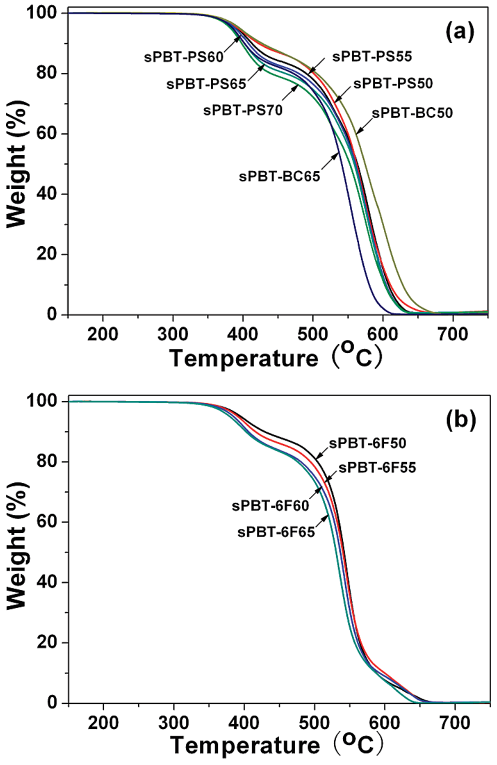

Figure 2. TGA curves of (a) sPBT-BC and sPBT-PS series and (b) sPBT-6F series.

IEC, Water Uptake, Swelling, and Proton Conductivity of sPBT. The IEC value of sPBT membranes is an important parameter when used as PEM.[3] The theoretical value of IEC of sPBT was calculated according to their molecular formulas, and the experimental value was obtained by titration. The results are compiled in Table 1. In all cases, the experimental value of IEC agrees with the theoretical one, indicating that the sulfonate groups were successfully incorporated into polymer backbone by polycondensation. The IEC value of sPBT membranes was adjusted in a range of 1.8−2.7 meq/g by varying

Table 2. Solubility of sPBT[a]

polymer	NMP	DMSO	DMF	DMAc	sulfolane	methanol	H_2O
sPBT-BC50	+−	+−	+−	+−	+−	−	−
sPBT-BC65	+−	+−	+−	+−	+−	−	−
sPBT-PS50	+	+	+	+−	+−	−	−
sPBT-PS55	+	+	+	+−	+−	−	−
sPBT-PS60	+	+	+	+−	+−	−	−
sPBT-PS65	+	+	+	+−	+−	−	−
sPBT-PS70	+	+	+	+−	+−	−	−
sPBT-6F50	+	+	+	+−	+−	−	−
sPBT-6F55	+	+	+	+−	+−	−	−
sPBT-6F60	+	+	+	+−	+−	−	−
sPBT-6F65	+	+	+	+−	+−	−	−

[a] The test was performed at a concentration of 0.05 g/mL. (+) soluble on heating; (+−) partially soluble or swelling on heating; (−) insoluble even on heating.

the feed ratios in order to ensure that they could exhibit high proton conductivity. The experimental value of IEC of sPBT-BC series was not obtained because they denoted low solubility and thus could not be cast into membranes.

According to the vehicle mechanism of proton transport, the membrane could not conduct proton unless it absorbs an appropriate amount of water, but excessive absorption of water would lead to too much swelling and even loss of mechanical strength.[3,14] Therefore, it is significant to investigate the water uptake and swelling of sPBT membranes in order to maintain the balance between the proton conductivity and mechanical properties. The water uptake of sPBT-6F and sPBT-PS series as functions of temperature and sulfonation degree is plotted in Figure 3. As shown, the water uptake of sPBT-PS membranes increased slowly up to 60 °C and thereafter increased more evidently with temperature, especially for those membranes with high sulfonation degree, wheras the water uptake of sPBT-6F membranes increased slowly in the whole temperature region. It could also be found that the water uptake of sPBT-PS membranes is higher than that of sPBT-6F membranes with an equivalent IEC at the same temperature. For example, sPBT-PS50 and sPBT-6F55 have an equal IEC (2.06 meq/g), but the former showed a water uptake of 43.6%, higher than that (36.9%) of the latter at 80 °C. The difference in water uptake between the sPBT-PS and -6F membranes is attributed to the difference in their structure. The hydrophobic nature of hexafluoroisopropylidene moieties might endow the sPBT-6F membranes with low water uptake. The sPBT-6F series showed a water uptake of 34.8−44.0% at 80 °C, slightly higher than that (30%) of Nafion 117.[14] At the same time, the sPBT-PS50, -PS55, and -PS60 membranes displayed a water uptake of 43.6−52.5% at 80 °C, higher than that of Nafion 117 but still lower than that (54%) of Dow membrane,[3,4] whereas the sPBT-PS65 and -PS70 membranes exhibited a water uptake of 61.9−69.1%. In addition, the water uptake values at 80 °C were expressed as the hydration number

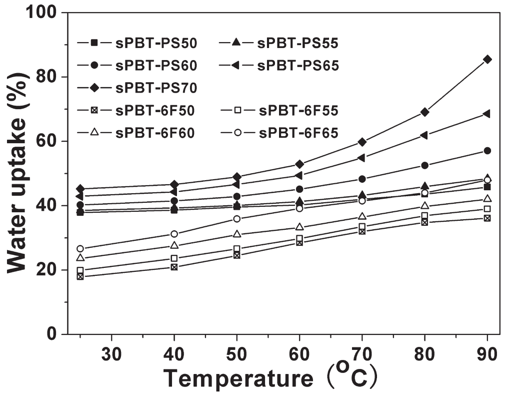

Figure 3. Water uptake of sPBT membranes at various temperatures.

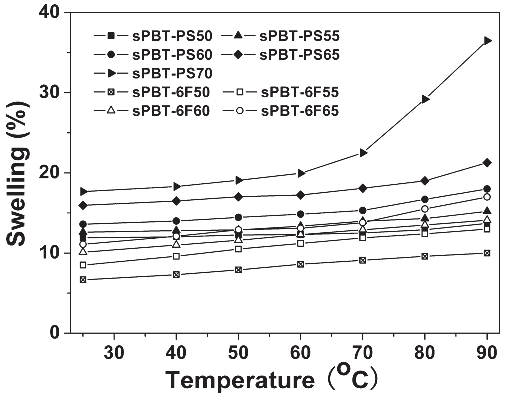

Figure 4. Swelling of sPBT membranes at various temperatures.

(λ), which was listed in Table 1. The hydration number is in the range of 10.0−14.2, close to that of other sulfonated aromatic polymers[22,59] and Nafion 117.[60]

The swelling of sPBT membranes as functions of temperature and sulfonation degree is displayed in Figure 4. Similar to the water uptake, the swelling increased as the temperature and sulfonation degree rise. At 80 °C, all the sPBT membranes, except for the sPBT-PS70 membrane, exhibited a swelling lower than that (20%) of Nafion 117,[14,18] showing excellent dimensional stability. As shown in Table 1, the sPBT-PS50−PS65 and sPBT-6F50−6F65 membranes indicate a high IEC of 1.89−2.55 meq/g, but they denote a low swelling. This might be ascribed to the strong intermolecular interaction between the sulfonic acid and thiazole rings.

In short, except for the sPBT-PS65 and -PS70, the sPBT-PS and sPBT-6F series showed moderate water uptake as well as low swelling, so they possessed excellent dimensional stability.

The proton conductivity of sPBT membranes was measured after they were fully hydrated in deionized water for 48 h. The proton conductivity of Nafion 117 and sPBT membranes against temperature is displayed in Figure 5. As expected, the proton conductivity increased with increasing temperature. At the same temperature, for each sPBT series, the proton conductivity enhanced

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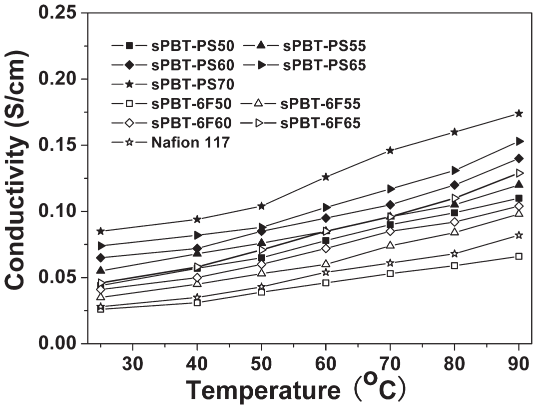

Figure 5. Proton conductivity of sPBT membranes at various temperatures.

with the increase in sulfonation degree. Nafion 117 showed a proton conductivity comparable to the previous value.[61,62] In the entire temperature range studied, all the sPBT membranes, except for sPBT-6F50 with the lowest IEC, showed higher proton conductivity than that of Nafion 117. At the same time, all the sPBT membranes, except for the sPBT-PS70 membrane, exhibited a swelling lower than that (20%) of Nafion 117 at 80 °C. Hence most of sPBT membranes displayed high proton conductivity as well as low swelling.

It could also be found that the sPBT-PS membranes showed higher conductivity than that of sPBT-6F membranes with an equal IEC. For example, both sPBT-PS50 and sPBT-6F55 showed an IEC of 2.06 meq/g, but the former possessed a proton conductivity of 0.10 S/cm while the latter denoted a proton conductivity of 0.08 S/cm at 80 °C. This might be due to the fact that sPBT-PS50 show higher water uptake as well as wider ionic channels than sPBT-6F55. The effect of ionic channels on the proton conductivity would be discussed in the last part.

Oxidative and Hydrolytic Stability of sPBT Membranes. Up to now, aromatic proton exchange membranes generally exhibited lower lifetime than perfluorinated membranes.[55] Therefore, the oxidative stability of aromatic PEM is especially important for fuel cell applications. The oxidative stability of sPBT membrane was evaluated by observing their dissolving behavior in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C according to a typical testing procedure.[55] The weight loss after treatment for 1 h and the elapsed time (τ) when the membrane samples dissolved completely are listed in Table 3. As shown, all the membranes retained more than 96% of their original weight and still kept their shape and flexibility after treatment for 1 h. The retained weight of sPBT polymers is comparable to or more than that of sulfonated poly(arylene ether ketone)s[63,64] and sulfonated polyimides.[55] Meanwhile, it could also be found that the sPBT-PS membranes exhibited an elapsed time of 2.0−4.0 h and that the sPBT-6F membranes showed an elapsed time of 3.5−5.5 h, which are also comparable to or more longer than the elapsed time of sulfonated poly(arylene ether ketone)s[63] and sulfonated polyimides[19,55] under the same conditions. Both sPBT series denoted high retained weight and long elapsed time, indicating high oxidative stability. On the other hand, their elapsed time and residue after 1 h treatment showed a decreasing tendency with increasing sulfonation degree like the previous report.[55] This illustrated that their oxidative stability decreased with sulfonation degree. In addition, the sPBT-PS50, -PS55, and -PS60 membranes displayed a retained weight of 98, 98, and 97% as well as an elapsed time of 4.0, 3.5, and 3.0 h, whereas the sPBT-6F55, -6F60, and -6F65 membranes denoted a residual weight of 99, 99, and 98% as well as an elapsed time of 5.0, 4.5, and 3.5 h, respectively. As shown in Table 1, the IEC value of sPBT-PS50, -PS55, and -PS60 membranes is equivalent to that of the sPBT-6F55, -6F60, and -6F65 membranes, respectively. Hence, these results (the residual weight and the elapsed time of membranes) demonstrated that the sPBT-6F membranes had a better oxidative stability than the sPBT-PS membranes with an equivalent IEC. The reasons might be as follows. First, the oxidative attack by the hydrated HO· and HOO· radicals occurred mainly in water-containing hydrophilic domains.[63] Second, the sPBT-PS membranes exhibited a higher water uptake than the sPBT-6F membranes with an equal IEC, the absorbed water facilitated the transport of HO· and HOO· radicals and thus enhanced the oxidative attack. In addition, the microstructure of sPBT membranes could affect their oxidative stability, which would be discussed in Microscopic Morphology.

Table 3. Oxidative Stability of sPBT Membranes in Fenton's Reagent

membrane	thickness (μm)	residue[a] (%)	τ^b (h)
sPBT-PS50	40	98	4.0
sPBT-PS55	43	98	3.5
sPBT-PS60	42	97	3.0
sPBT-PS65	40	97	2.5
sPBT-PS70	41	96	2.0
sPBT-6F50	39	99	5.5
sPBT-6F55	40	99	5.0
sPBT-6F60	42	98	4.5
sPBT-6F65	38	97	3.5

[a] Residual weight of membranes after treatment in Fenton's reagent for 1 h. [b] τ refers to the time when the membrane dissolved completely.

The hydrolytic stability of PEM is also important because it works in the hydrothermal environment.[19] Most sulfonated polyimide membranes were characterized in terms of hydrolytic stability. This is probably because the imide groups of sulfonated polyimides exhibited lower hydrolytic stability compared with the functional groups, such as aromatic ether, phosphazene, and benzimidazole groups of other sulfonated polymers.[8,23,31] In contrast, few other sulfonated aromatic PEM have been characterized in terms of hydrolytic stability. Because sPBT-based proton exchange membranes have not been reported until now, their hydrolytic stability should be investigated in

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Table 4. Hydrolytic Stability of sPBT Membranes

			mechanical property[a]			GPC			
membrane	IEC (meq/g)	time (h)	tensile strength (MPa)	Young's modulus (GPa)	elongation at break (%)	Mn × 10^{-4} (g/mol)	M_w × 10^{-4} (g/mol)	PDI	weight loss (%)
sPBT-PS50	2.06	0	75.1	1.51	49.4	9.89	18.7	1.89	0
		2	68.1	1.41	33.6	10.1	19.3	1.91	1
		24	66.1	1.38	32.7	10.7	20.9	1.94	2
sPBT-PS55	2.22	0	74.7	1.31	48.5	8.51	13.8	1.63	0
		2	65.1	1.29	31.2	8.82	14.9	1.69	2
		24	61.2	1.30	28.4	9.64	16.7	1.73	3
sPBT-PS60	2.39	0	79.2	1.62	39.3	13.8	30.3	2.18	0
		24	75.2[b]	1.59[b]	30.1[b]	15.3	39.7	2.61	-[c]
sPBT-6F55	2.06	0	71.5	1.13	27.8	12.1	29.1	2.41	0
		24	69.9	1.15	21.3	12.2	29.9	2.46	1
sPBT-6F60	2.23	0	73.8	1.19	30.1	11.2	28.0	2.50	0
		24	67.9	1.21	25.3	11.6	29.7	2.56	1
sPBT-6F65	2.40	0	80.6	1.34	30.5	12.3	30.1	2.44	0
		24	75.7	1.33	27.8	12.5	32.1	2.57	1

[a] The wet samples were equilibrated at 50% RH and 25 °C for 1 day. [b] The data were obtained by measuring the membrane recast from its residue after aging test. [c] have not been measured due to excessive swelling.

detail so as to determine whether they are suitable for fuel cell applications or not. Following a recent procedure,[55] the sPBT membranes were investigated in water at 140 °C for 24 h as an accelerated aging test; the hydrolytic stability was evaluated by changes in appearance, mechanical properties, residual weight, molecular weight, ^{1}H NMR spectra, and IR spectra before and after the testing. Three samples of sPBT-PS series (sPBT-PS50, -PS55, and -PS60) and three samples of sPBT-6F series (sPBT-6F55, -6F60, and -6F65) exhibited high proton conductivity as well as low swelling, and thus their hydrolytic stabilities were evaluated as typical examples. After the aging test, all the membranes except for sPBT-PS60 maintained their transparency, flexibility, and toughness in appearance. Table 4 lists the mechanical properties, residual weight, and molecular weight before and after the aging test. As shown, sPBT-PS50 and -PS55 exhibited little decrease in tensile strength, Young's modulus, and elongation at break after 24 h aging test. Interestingly, the decrease in mechanical properties took place mainly in the initial period of aging (2 h). The amplitude of decrease in the initial aging for 2 h is much higher than that in the subsequent aging for 22 h. It is well-known that sulfonated polymers indicated a hydrophobic/hydrophilic nanophase separation morphology. The hydrophilic domains absorbed water and swelled under the harsh hydrothermal conditions, so the membrane might undergo an irreversible change of microstructure in the initial aging as in ref 8, whereas the possible hydrolysis might increase gradually with time. Hence the decrease in mechanical properties might mainly result from the microstructural change of the membranes. On the other hand, the sPBT-PS50 and -PS55 membranes lost 2−3% of their original weight, whereas the aromatic PEM with the longest lifetime reported still lost 8% of its original weight after the same aging test.[55] Therefore, the sPBT-PS50 and -PS55 membranes possessed high hydrolytic stability. In addition, their molecular weight after treatment showed a slight increase, probably due to the fact that a small part with low molecular weight in samples might dissolve in deionized water during the testing. Different from the sPBT-PS50 and -PS55 membranes, the sPBT-PS60 membrane swelled excessively after aging for 24 h and could not be characterized in terms of mechanical properties, but the membrane recast from its residue almost retained the initial mechanical properties, as shown in Table 4. This result further illustrated that the sPBT-PS membranes had excellent hydrolytic stability. In the case of sPBT-6F series membranes, the amplitude of decrease in tensile strength, elongation at break, and residual weight is even less than that of sPBT-PS series membranes with an equivalent IEC. Moreover, their Young's modulus and molecular weight after aging test almost remained intact. In other words, the sPBT-6F membranes displayed better resistance to hydrolysis in comparison with the sPBT-PS membranes containing an equal IEC.

As typical examples, a group of sPBT membranes (sPBT-PS50 and -6F55) after the hydrothermal aging for 24 h were analyzed in terms of ^{1}H NMR and IR spectroscopy to detect their structural change. The ^{1}H NMR and IR spectra of the treated sPBT polymers hardly exhibited any difference compared with those of the pristine polymers [see Figure S4−S5 in the Supporting Information]. These results further demonstrated that the sPBT-PS and sPBT-6F membranes possessed excellent hydrolytic stability.

Microscopic Morphology. The macroscopic properties of proton exchange membranes, such as water uptake, swelling, proton conductivity, oxidative stability, and hydrolytic stability, are greatly affected by their microstructure.[3,14] The microscopic morphology of sPBT membranes was investigated by atomic force microscopy (AFM). As typical examples, the tapping mode AFM phase images for three samples of sPBT-PS series and three samples of sPBT-6F series were recorded under ambient conditions on a 500 nm × 500 nm size scale, as shown in Figure 6. All the AFM images exhibited a dark/bright nanophase separation morphology. The dark regions are assigned to hydrophilic ionic clusters

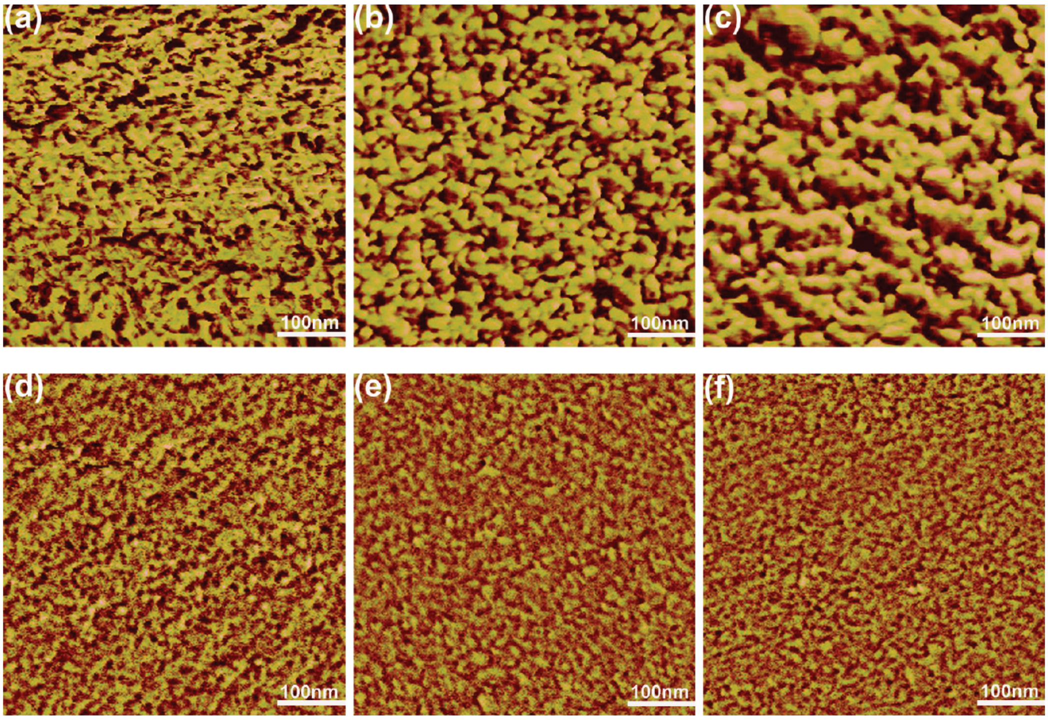

Figure 6. AFM images of (a) sPBT-PS50, (b) sPBT-PS55, (c) sPBT-PS60, (d) sPBT-6F55, (e) sPBT-6F60, and (f) sPBT-6F65.

containing small amounts of water, whereas the bright areas are attributed to hydrophobic polymer backbone.[3,65] In general, the hydrophilic channels absorb water and are responsible for proton transport, whereas the hydrophobic domains provide the ionomers with morphological stability and keep them from dissolving in water.[3,63,66] The sPBT-PS series (sPBT-PS50, -PS55, and -PS60) showed a typical nanophase separation morphology like most of sulfonated aromatic polymers,[67] i.e., the size and connectivity of hydrophilic ionic channels exhibited an increasing tendency with degree of sulfonation. It is well-known that the oxidative and hydrolytic degradation occurred mainly in water-containing hydrophilic domains.[63] Hence the water uptake, swelling, and proton conductivity enhanced but the oxidative and hydrolytic stability decreased with increasing degree of sulfonation. When the sulfonated repeat unit of sPBT-PS series is at 60 mol %, the size and connectivity of hydrophilic channels reached a critical limit, wherein the corresponding membrane (sPBT-PS60) underwent excessive swelling in water at 140 °C for 24 h. In contrast, the sPBT-6F membranes (sPBT-6F55, -6F60, and -6F65) displayed a particular morphology, much different from that of sPBT-PS membranes. In other words, they showed much narrower ionic channels in comparison with the sPBT-PS membranes with an equivalent IEC. The connectivity of ionic channels enhanced but their size exhibited a slightly decreasing tendency increase with degree of sulfonation. These results are due to the hydrophobic and flexible hexafluoropropylidene moieties. Similar results were observed in other sulfonated polymers containing bulky hydrophobic moieties.[66] For the ionomer membranes, the narrow ionic channels receive more strong binding arising from the surrounding hydrophobic domains in comparison with the wide ones. This led to the result that the narrow ionic channel-containing ionomer membranes indicated higher dimensional stability (or lower swelling) than the wide ionic-channel-containing ionomer membranes with an equivalent IEC.[66] For example, the sPBT-6F65 and sPBT-PS60 membranes have an equal IEC, but the former showed narrower ionic channels than the latter, as indicated in Figure 6. Therefore, the sPBT-6F65 membrane still denoted a tensile strength of 75.7 MPa after the hydrolytic test, whereas the sPBT-PS60 membrane swelled excessively and almost lost its mechanical strength under the same conditions as mentioned above. That is to say, the former showed much better dimensional stability than the latter. Similarly, the narrow ionic channels-containing sPBT-6F membranes exhibited higher oxidative and hydrolytic stability than the wide ionic channels-containing sPBT-PS membranes with an equivalent IEC, because the oxidative and hydrolytic degradation occurred mainly in hydrophilic domains containing absorbed water.[63] Therefore, the incorporation of the hydrophobic and flexible hexafluoroisopropylidene moieties to the backbone of sulfonated polymers could enhance their dimensional, oxidative, and hydrolytic stability. This provided an approach for improving the properties of proton exchange membranes.

As shown in Figure 5, the sPBT-6F membranes exhibited lower proton conductivity than the sPBT-PS membranes with an equal IEC. For instance, the sPBT-6F55, -6F60,

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and -6F65 membranes indicated lower proton conductivity than the sPBT-PS55, -PS60, and -PS65 membranes, respectively. The reason is that the sPBT-6F membranes showed much narrower ionic channels along with lower water uptake than the sPBT-PS membranes with an equivalent IEC. Even so, the sPBT-6F55, -6F60, and -6F65 membranes still exhibited a proton conductivity higher than that of Nafion 117.

Conclusions

Three series of high-molecular-weight sulfonated polybenzothiazoles (sPBT) were successfully synthesized by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride with bis(3-sulfonate-4-carboxyphenyl) sulfone and bis(4-carboxyphenyl) sulfone or diphenyl sulphone-2,5-dicarboxylic acid or 2,2-bis(4-carboxyphenyl)hexafluoropropane. The sPBT-BC series showed poor solubility, while the sPBT-PS and sPBT-6F series exhibited excellent solubility in organic solvents such as NMP, DMSO, and DMF. The incorporation of the phenylsulfonyl pendant groups or hexafluoroisopropylidene moieties to the resulting sPBT greatly enhanced the solubility. High-molecular-weight sulfonated polybenzothiazoles with excellent solubility were synthesized for the first time. Such sulfonated polybenzothiazoles thus could be cast into homogeneous membranes and could be further evaluated as proton exchange membranes. All the sPBT showed high thermal stability, the T_{d5} of which is no lower than 380 °C. Except for the sPBT-PS70 membranes, the sPBT-PS and sPBT-6F series indicated high proton conductivity as well as low swelling. For example, sPBT-PS55 and sPBT-6F65 exhibited a proton conductivity of 0.105 and 0.11 S/cm at 80 °C, respectively, much higher than that of Nafion 117. However, they showed a swelling of only 14.3 and 15.5% at 80 °C, respectively, indicating high dimensional stability. In addition, these sPBT membranes exhibited high oxidative stability and excellent hydrolytic stability. AFM images revealed that the sPBT polymers presented an increasing hydrophilic/hydrophobic nanophase separation morphology with degree of sulfonation. Thus their water uptake, swelling, and proton conductivity increased but their oxidative and hydrolytic stability decreased with degree of sulfonation. For the sPBT-PS membranes, the size and connectivity of hydrophilic ionic channels enhanced with degree of sulfonation like most of sulfonated polymers. In contrast, the sPBT-6F membranes denoted much narrower ionic channels than the sPBT-PS membranes with an equivalent IEC because of the hexafluoroisopropylidene moieties, so the former displayed better dimensional stability, oxidative stability, and hydrolytic stability than the latter. As a result, sulfonated polybenzothiazoles are a novel candidate for PEM materials. More sPBT membranes with various structures would be prepared in our future studies.

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Supporting Information Available: The assignment analysis of ^{1}H NMR spectra of sPBT-6F65, sPBT-BC65, and sPBT-PS65; FT-IR spectra of all the sPBT polymers; DSC curves of the acid form sPBT; ^{1}H NMR and FT-IR spectra of the membranes (sPBT-PS50 and sPBT-6F55) before and after the hydrolytic testing (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.